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ELECTROCHEMICAL BEHAVIOUR AND CHEMICAL OXIDATION STUDY OF THIO- AND PHOSPHIDO-BRIDGED BINUCLEAR IRON COMPLEXES

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Summary

The electrochemical behaviour of thio and phosphido complexes of iron(I): $Fe_2XY(CO)_{6-n}L_n$ ($X = Y = SR, PR_2$ and $X = SR$, $Y = PR_2$, $L = PR_3$) has been studied on platinum and mercury electrodes, in organic solvent. These complexes are reduced in a two-electron irreversible process. A large difference is observed between their oxidation potentials on mercury and platinum electrodes; this is ascribed to the formation of a mercury complex in which mercury is inserted into the metal—metal bond. In oxidation on platinum electrodes, two monoelectronic waves are observed. The influence of the ligand basicity on the cathodic $E_{1/2}$ values is discussed. A parallel shift is observed between the $E_{1/2}$ and the IR ν(CO) of the totally symmetrical mode. Chemical oxidation of the complexes shows that the dications cannot be isolated, and leads to isolation of the following species: $[FeP(CH_3)_2(CO)_3]_2AgNO_3$, $[FeSCH_3(CO)_2P(CH_3)_3]_2(NO_3)_2$, $\{[FeSCH_3(CO)_2P(CH_3)_3]_2F\}PF_6$, where NO_3^- and F^- act as ligands.

I. Introduction

Several papers have been devoted to the study of thio- and phosphido-bridged iron compounds, $[FeSR(CO)_3]_2$ and $[FePR_2(CO)_3]_2$, having a metal—metal bond between the two iron atoms [1—8].

Dessy and his colleagues [7] used a mercury electrode in 1,2-dimethoxyethane containing 0.1 *M* $(C_4H_9)_4NClO_4$ with Ag/0.1 *M* Ag^+ as reference electrode and concluded that the mechanism of reduction of $[FeSCH_3(CO)_3]_2$ was as in eq. 1,

$$[FeSCH_3(CO)_3]_2 + e \rightarrow [FeSCH_3(CO)_3]_2^{-}$$

$$E_{1/2} - 1.9\ V \qquad (1)$$

TABLE 1

PHYSICAL AND ANALYTICAL DATA FOR THE PRODUCTS OBTAINED BY CHEMICAL OXIDATION OF THE INITIAL IRON COMPLEXES

Complex	Yield (%)	Colour	M.p. (°C)	Λ_M (Ohm^{-1} cm^2 mol^{-1})	Analysis (Found (calcd.) (%))					
					C	H	P	N	Ag	F
$[FeP(CH_3)_2(CO)_3]_2AgNO_3$	60	yellow	95 [a]	6.2	21.14 (20.97)	2.16 (2.09)	10.80 (10.83)	2.52 (2.44)	18.12 (18.84)	
$[FeSCH_3(CO)_2P(CH_3)_3]_2(NO_3)_2$	47	yellow	110 [a]	29.6	24.44 (24.24)	4.08 (4.04)	10.59 (10.43)	4.76 (4.71)		
$\{[FeSCH_3(CO)_2P(CH_3)_3]_2F\}PF_6$	50	orange	112 (dec)	116	22.40 (22.71)	3.72 (3.78)	14.73 (14.66)			20.50 (20.97)

[a] Crystals explode at this temperature.

and that the generated radical anion can be reoxidized after exhaustive reduction, to give back the starting material. Process 1 was followed by an ill-defined monoelectronic polarographic wave. In the same publication, Dessy et al. show that $[FeP(CH_3)_2(CO)_3]_2$ is reduced almost reversibly at $E_{1/2}$ — 2.0 V into the stable dianion, according to eq. 2.

$$[FeP(CH_3)_2(CO)_3]_2 + 2\,e \rightarrow [FeP(CH_3)_2(CO)_3]_2^{2-} \qquad (2)$$

They also show that $[FeP(CH_3)_2(CO)_3]_2$ is not oxidizable on mercury electrode. This difference between the reactions 1 and 2 for very similar complexes is surprising, because the only differences between the starting materials are the thio and phosphido bridges. Results on related complexes have been described [8—11]. Also, Hieber et al. [12] demonstrated that chemical reduction of $[FeS(C_6H_5)(CO)_3]_2$ with $NaBH_4$ or Na(Hg) destroys the complex, polynuclear carbonyl ferrates and mercaptans being obtained.

In the present work, several iron(I) thio and phosphido-bridged complexes have been studied electrochemically and the influence of various iron substituents on the redox reactivity of the complexes analyzed. For comparison with the results obtained in electrochemical oxidation we tried to obtain similar cations by chemical oxidation of the initial complexes with $AgNO_3$ and $AgPF_6$.

II. Experimental

1. Chemical procedure

All the reactions were performed under nitrogen. IR spectra were recorded on a Perkin—Elmer 225 spectrometer in CH_2Cl_2 and proton NMR spectra on a Varian A60A. The conductivity measurements were carried out at room temperature in acetone (10^{-3} *M* solution) with a Philips conductimeter.

A commercial sample of compound $[FeSCH_3(CO)_3]_2$ (Pressure Company) was used without further purification. $[FeP(CH_3)_2(CO)_3]_2$ and $[FeP(C_6H_5)_2(CO)_3]_2$ were prepared by published procedures [13,14]. $Fe_2S(C_6H_5)P(C_6H_5)_2(CO)_6$, first described by Thompson et al. [14] was synthesized by a different method, involving UV irradiation with a high pressure mercury vapor lamp (Original Hanau TQ 150) of a mixture of 2 mol of $Fe(CO)_5$ with 1 mol of $P(C_6H_5)_2S(C_6H_5)$ in benzene, which gives the dinuclear complex in 35% yield. $[FeS(C_6H_5)(CO)_3]_2$ was prepared by treatment of $Fe_2(CO)_9$ with C_6H_5SH at room temperature [15], and $[FeSCH_3(CO)_2P(CH_3)_3]_2$ was synthesized by a published procedure [16].

The chemical oxidations were performed in acetone with $AgNO_3$ and $AgPF_6$, the stoechiometry iron complex/oxidant being 1/2. The products were purified by crystallisation from a dichloromethane/ether mixture. The elemental analyses and the physical properties of the products are listed in Table 1.

2. Electrochemical measurements

Electrochemical studies were carried out using a PRG 4 device from S.O.L.E.A. (cathodic range) and a potentiostat (S.O.L.E.A. PRT 20 2X) coupled to a signal generator (GSATP, S.O.L.E.A.) (anodic range). The potentials were measured vs. a saturated calomel electrode (SCE) at room temperature, and their accuracy was ±10 mV. The SCE was connected to the organic solution by a salt bridge containing the solvent and the supporting electrolyte (propylene carbonate + KPF_6 or $(C_6H_{13})_4NClO_4$ 0.05 *M*) as described elsewhere [17—19]. The solvent propylene carbonate was distilled under reduced pressure at 95°C under argon. The supporting electrolyte was either tetra-n-hexylammonium perchlorate (cathodic measurements) or potassium hexafluorophosphate (anodic studies). These salts were recrystallized before use and dried and stored under a dry inert atmosphere. Each solution was degassed with dry argon for 30 min, before polarization. A dropping mercury electrode (DME) was used in normal pulse polarography, the most cathodic potential obtainable being —2.9 V/SCE in propylene carbonate + 0.05 *M* $(C_6H_{13})_4NClO_4$. The capillary used had a flow rate of 0.5 mg s^{-1}, for 35 cm of mercury above the capillary tip. A platinum rotating disk electrode or platinum stationary electrodes was used for the anodic investigations in propylene carbonate + 0.005 *M* KPF_6. The auxiliary electrode in both studies was a Pt foil. The rotating rate of the platinum disk electrode was 3000 rpm and the potential scan rate 0.001 V/s. When the stationary platinum electrode was used for cyclic voltammetry the potential scan rate ranged from 0.3 to 3 V/s. The number of Faradays involved per mol of reactant in the electrochemical reactions was determined by potentiostatic coulometry and by comparison of the wave heights with the height of the well known ferrocene/ferricinium couple ($E_{1/2}$ + 0.40 V/SCE, internal reference). Exhaustive electrolyses were carried out at potentials at least 50 mV more anodic or cathodic than the corresponding plateau potential of the wave.

III. Results

1. *Electrochemical reductions on mercury electrode*

All the complex studied are polarographically reducible in a well-defined cathodic wave. The half-wave potentials $E_{1/2}$ measured in propylene carbonate and $(C_6H_{13})_4NClO_4$ are listed in Table 2, together with the number of Faradays exchanged per mol of electroactive species ($n = 2$ for all species). The $E_{1/2}$'s were measured by normal pulse polarography. For each complex, the number of electrons involved in the cathodic process is two. The most easily reducible complex is $[FeS(C_6H_5)(CO)_3]_2$ ($E_{1/2}$ — 0.98 V/SCE), and the most difficult to reduce $[FeSCH_3(CO)_2P(CH_3)_3]_2$ ($E_{1/2}$ — 2.1 V/SCE). For all polarographic waves (normal pulse polarography) the limiting current was found to be proportional to the concentration of the complex, and the chronoamperometric criterion [20] showed that the limiting current is diffusion controlled. After exhaustive reduction of these complexes at potentials on the plateau of the respective polarographic cathodic waves, followed by reoxidation, the starting material was not recovered in contrast to the results obtained by Dessy et al. [7].

On the other hand, the results obtained in cyclic voltammetry and by reversal normal pulse polarography are consistent with an electrochemical non-reversible process complicated by following chemical reactions: the cyclic voltammograms of the complexes show a cathodic peak whose current peak is higher than the corresponding anodic value, and the difference ΔE_p is higher than the 30 mV expected for a reversible two-electron process. It thus can be assumed that after addition of two electrons to the complexes, dianions are obtained, and that these undergo further chemical reactions as proposed by Hieber et al. [12].

2. *Electrochemical reduction on platinum electrode*

On stationary and rotating platinum electrodes, the complexes are reduced in two electron processes, as on the mercury electrode. The cathodic peak potentials, E_p, obtained by cyclic voltammetry are listed in Table 2. The number of Faradays exchanged per mol of electroactive species ($n = 2$) was determined by comparing the height of the cathodic wave on a rotating disk electrode with that of the wave of the ferrocene/ferricinium redox couple. As shown in Table 2, the E_p values on platinum are close to the corresponding cathodic $E_{1/2}$ values on mercury.

3. *Electrochemical oxidation on mercury electrode*

In propylene carbonate and 0.05 M $(C_6H_{13})_4NClO_4$, the anodic limit on a DME is +0.8 V/SCE. Under these conditions only $[FeSCH_3(CO)_3]_2$, $[FeSCH_3(CO)_2P(CH_3)_3]_2$ and $[FeP(CH_3)_2(CO)_3]_2$ are oxidized, and these exhibit an anodic wave at $E_{1/2}$ +0.70, +0.30, and +0.42 V/SCE, respectively. These anodic waves are irreversible and diffusion controlled. The complexes $Fe_2S(C_6H_5)P(C_6H_5)_2(CO)_6$, $[FeS(C_6H_5)(CO)_3]_2$ and $[FeP(C_6H_5)_2(CO)_3]_2$ are not oxidized on mercury under these conditions.

By potentiostatic coulometry of $[FeS(CH_3)(CO)_3]_2$ and $[FeSCH_3(CO)_2P(CH_3)_3]_2$ it was shown that one Faraday per mol is exchanged in the oxidation step, whereas two Faradays are exchanged per mol of $[FeP(CH_3)_2(CO)_3]_2$. Cyclic voltammetry demonstrates that these anodic oxidations are not reversible (no cathodic peaks).

4. *Electrochemical oxidation on platinum electrode*

The measurements were carried out on a rotating platinum disk electrode in propylene carbonate and 0.05 M KPF_6. All the complexes are oxidized in two irreversible monoelectronic steps. In cyclic voltammetry on a stationary (rotating disk) platinum electrode, two anodic peaks are observed for each complex, the first (the less anodic) exhibiting a corresponding cathodic peak and the second no such peak. The anodic peaks values E_{p_a} are so different from the corresponding $E_{1/2}$ obtained on mercury (Table 2) that it is resonable to suspect that a chemical reaction takes place between the mercury and the complexes. It is known that salts of mercury(II) react with $[FeP(CH_3)_2(CO)_3]_2$ and $[FeSCH_3(CO)_2P(CH_3)_3]_2$ [27], mercury being inserted between the two iron atoms. Similar reactions between mercury and iridium complexes have been observed by Vlcek et al. [21,22]. Compared to the other complexes, the anodic peak values for $[FeP(CH_3)_2(CO)_3]_2$ are close together on platinum ($E_{p_{a1}}$ + 1 V and $E_{p_{a2}}$ + 1.4 V/SCE). Thus, the existence of a unique bielectronic-anodic wave on the mercury electrode could be a consequence of a chemical reaction between the mercury and the initial complex. The nature of the species resulting from exhaustive electrolysis on a mercury electrode is under study, but the presence of mercury in these compounds has been established [28].

IV. Discussion of the electrochemical results

Under the conditions described the complexes $Fe_2XY(CO)_{6-n}L_n$ are electrochemically reduced in a two electron step, leading to the dianion not the mono-

TABLE 2

RESULTS FROM POLAROGRAPHY, COULOMETRY AND CYCLIC VOLTAMMETRY ON BRIDGED DIMERIC IRON(I) COMPLEXES

(Cathodic results obtained in propylene carbonate +0.05 M $(C_6H_{13})_4NClO_4$ and anodic results in propylene carbonate +0.05 M KPF_6)

Compound		Anodic range				Cathodic range			
		Mercury electrode		Platinum electrode		Mercury electrode		Platinum electrode (0.2 V/s)	
		$E_{1/2}$	n[a]			$E_{1/2}$	n[a]		
$[FeSCH_3(CO)_3]_2$	(III)	+0.70 V	1	Ep_{a1} +1.20 V Ep_{a2} +2.00 V	$n = 1$ $n = 1$	−1.22 V	2	Ep_c −1.26 V	$n = 2$
$[FeSCH_3(CO)_2P(CH_3)_3]_2$	(VI)	+0.30 V	1	Ep_{a1} +0.10 V Ep_{a2} +1.90 V	$n = 1$ $n = 1$	−2.10 V	2	Ep_c −2.20 V	$n = 2$
$[FeP(CH_3)_2(CO)_3]_2$	(V)	+0.42 V	2	Ep_{a1} +1.00 V Ep_{a2} +1.40 V	$n = 1$ $n = 1$	−1.60 V	2	Ep_c −1.54 V	$n = 2$
$Fe_2S(C_6H_5)P(C_6H_5)2(CO)_6$	(II)	no wave		Ep_{a1} +1.15 V Ep_{a2} +2.30 V	$n = 1$ $n = 1$	−1.12 V	2	Ep_c −1.44 V	$n = 2$
$[FeS(C_6H5)(CO)_3]_2$	(I)	no wave		Ep_{a1} +1.26 V Ep_{a2} + 2.40 V	$n = 1$ $n = 1$	−0.98 V	2	Ep_c −0.96 V	$n = 2$
$[FeP(C_6H_5)_2(CO)_3]_2$	(IV)	no wave		Ep_{a1} +1.10 V Ep_{a2} +2.20 V	$n = 1$ $n = 1$	−1.27 V	2	Ep_c −1.24 V	$n = 2$

[a] n = number of Faradays exchanged per mol of electroactive species.

anion [7]. The respective $E_{1/2}$ values on DME or on platinum electrode become more cathodic in the following sequence: $[FeS(C_6H_5)(CO)_3]_2$(I) > $Fe_2S(C_6H_5)P(C_6H_5)_2(CO)_6$(II) > $[FeSCH_3(CO)_3]_2$(III) > $[FeP(C_6H_5)_2(CO)_3]_2$(IV) > $[FeP(CH_3)_2(CO)_3]_2$(V) >> $[FeSCH_3(CO)_2P(CH_3)_3]_2$(VI). This sequence parallels the increasing basicity of the ligands. Two types of ligands are coordinated to iron in the studied complexes viz. (i) bridging ligands such as SR or PR_2 (R = CH_3, C_6H_5), and (ii) non-bridging ligands such as CO or $P(CH_3)_3$.

First, we note that the non-bridging ligands have the strongest influence on the $E_{1/2}$ value (compare for instance III and V with VI). Secondly, among the bridging ligands the basicity scale is well respected (see for example V and III, IV and I), but these ligands have a smaller effect on $E_{1/2}$ than the non-bridging ligands. As already observed in similar cases [29], the shifts of the $E_{1/2}$ or E_{p_c} values parallel the changes in the IR ν(CO) frequencies of the totally symmetrical CO vibration mode (Table 3).

V. Results and discussion of the chemical oxidation of the complexes

Attempts to prepare the dications (presumably generated by the electrochemical oxidation) by chemical oxidation with Ag^+ salts (nitrates and hexafluorophosphates) failed, but new oxidation products were identified and are described below. In agreement with the results obtained by McCleverty et al. [23], no reaction was observed between $[FeSCH_3(CO)_3]_2$ or $[FeS(C_6H_5)(CO)_3]_2$ and Ag^+ salts. Also $Fe_2S(C_6H_5)P(C_6H_6)_2(CO)_6$ was recovered unaltered after attempted chemical oxidation by Ag^+ salts. Chemical oxidation of $[FeP(CH_3)_2(CO)_3]_2$ occurs with no precipitation of a silver mirror, but the silver salts dissolve. In the case of $AgNO_3$ it was possible to isolate the product of the reaction; and it has an analysis corresponding to $[FeP(CH_3)_2(CO)_3]_2AgNO_3$(VII). In the case of the $AgPF_6$ salt the same type of complex is indicated by the IR data (Table 3), but it could not be isolated because of its unstability. (The product darkened in solution or in solid state). With silver(I) salts, $[FeP(C_6H_5)_2(CO)_3]_2$ seems to give a complex of type VII, but the reaction reaches an equilibrium and attempts to isolate the species produced by the reaction with silver salts always gave a mixture of starting material with the silver adduct. Silver salts also react with $[FeSCH_3(CO)_2P(CH_3)_3]_2$ producing a silver mirror and yielding the products VIII and IX, which were isolated: $[FeS(CH_3)(CO)_2P(CH_3)_3]_2(NO_3)_2$(VIII), $\{[FeS(CH_3)(CO)_2P(CH_3)_3]_2F\}PF_6$(IX).

The possible structures of products VII, VIII and IX are now considered. The IR data in the ν(CO) stretching region and the proton NMR parameters are listed in Table 3. The IR spectrum of $[FeP(CH_3)_2(CO)_3]_2AgNO_3$(VII) is very similar to that of the compounds $[FeP(CH_3)_2(CO)_3]_2RC{\equiv}CR$ in which the alkyne is inserted into the metal—metal bond [24]. This suggests that the Ag^+ cation may be inserted into the metal—metal bond. This hypothesis is also supported by the observation of two PCH_3 resonances for the bridges, in the proton NMR spectrum. Furthermore product VII is non-conducting in acetone and the IR spectrum confirms that NO_3^- acts as a ligand [26] ($\nu(NO_3)$ (cm^{-1}): 1450, 1360, 1260, 1015), so the NO_3^- anion is certainly bonded to the silver. The thio-bridged complex VIII $[FeSCH_3(CO)_2P(CH_3)_3]_2(NO_3)_2$ shows three IR active

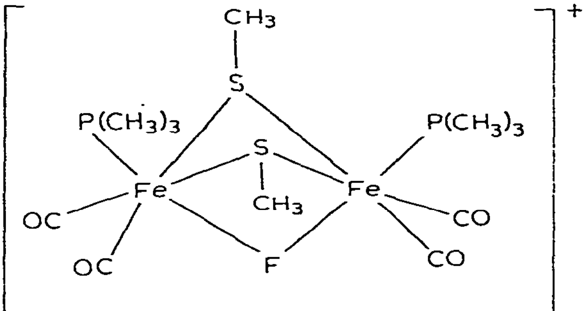
TABLE 3

INFRARED DATA FOR THE INITIAL COMPLEXES (I TO VI), INFRARED AND NMR DATA FOR CHEMICALLY PREPARED (VII TO IX) COMPLEXES, AFTER REACTION WITH SILVER(I) SALTS

Complexes	No	IR ν(CO) (cm^{-1})			
$[FeSC_6H_5(CO)_3]_2$	(I)	2075 ms	2039 vs	2007 s	1998 s
$Fe_2SC_6H_5P(C_6H_5)_2(CO)_6$	(II)	2064 s	2026 vs	1998 s	1981 s
$[FeSCH_3(CO)_3]_2$	(III)	2073 ms	2037 vs	2002 s	1992 s [a]
		2071 w	2037 vs	1998 m	1990 m [b]
$[FeP(C_6H_5)_2(CO)_3]_2$	(IV)	2053 ms	2015 s	1994 vs	1067 vs
$[FeP(CH_3)_2(CO)_3]_2$	(V)	2047 ms	2007 s	1977 vs	1963 vs
$[FeSCH_3(CO)_2P(CH_3)_3]_2$	(VI)	1988 s	1943 m	1923 s	*b*
$[FeP(CH_3)_2(CO)_3]_2AgNO_3$	(VIII)	2064 m	2037 s	2000 sh	1994 s
$[FeP(CH_3)_2(CO)_3]_2AgPF_6$		2065 w	2040 s		1995 s
$[FeP(C_6H_5)_2(CO)_3]_2AgNO_3$		2062 w	2038 s		1993 s
$[FeP(C_6H_5)_2(CO)_3]_2AgPF_6$		2065 w	2042 s		1995 s
$[FeSCH_3(CO)_2P(CH_3)_3]_2(NO_3)_2$	(VIII)	2048 m	2038 s		1994 s
$[FeSCH_3(CO)_2P(CH_3)_3]_2F]PF_6$	(IX)	2055 sh	2043 s		1998 s

[a] *Anti* isomer. [b] *Syn* isomer.

bands in the ν(CO) stretching region, which means that the C_{2v} symmetry of the starting material [16] is preserved. This is confirmed by the proton NMR spectrum, which shows that the two phosphines are equivalent and that the two SCH_3 are "*syn*" disposed. Complex IX also exhibits three ν(CO) IR active bands, but the proton NMR spectrum indicates that the two SCH_3 groups are non-equivalent. For the $P(CH_3)_3$ resonance there are two doublets of equal intensity separated by 1 Hz. This can be explained by assuming for IX a structure analogous to that proposed by Haines et al. [25] for $[Fe(CO)_2LSRX]^+$ (X = Br, I), in which the X group bridges the two iron atoms and the ligands L are *trans* oriented with respect to the X bridges. In the present case the two doublets for the $P(CH_3)_3$ proton NMR resonance would result from the coupling with the F nucleus. Thus the structure shown may be proposed for complex IX. Such a structure seems to be confirmed by conductivity measurements, which show that complex IX behaves as a 1/1 electrolyte in acetone. In contrast, solutions of complex VIII



(IX)

Proton NMR parameters

$\delta(P(CH_3)_2)$	$J(PH)$ (Hz)	$\delta(SCH_3)$	$J(PSH)$ (Hz)	$\delta(P(CH_3)_3)$	$J(PH)$ (Hz)	$J(FH)$ (Hz)
−1.71	12					
−1.76	12					
		−1.89	3.6 (t)	−1.39	10.4	
		−2.26	3 (t)	−1.51	10.6	1
		−2.90	1 (t)			

(Table 3) are non-conducting and the NO_3^- ions must be coordinated to the iron atoms in this case because the $\nu(NO_3)$ bands are in the same region as for complex VII (1465, 1350, 1250, 998 cm^{-1}). It is difficult to decide whether NO_3^- acts as a mono- or bi-dentate ligand, but the absence of dissociation of VIII in acetone seems to indicate that each NO_3^- is bonded in a unidendate formation to one iron atom. The study has also demonstrated that the dication $[FeSCH_3(CO)_2P(CH_3)_3]^{2+}$ cannot be isolated by a chemical route under the above conditions. This is explained by the fact that in this dication each iron is unsaturated, with only sixteen electrons in its coordination sphere, and achieves its coordination sphere either by coordination with the anion, when this anion exhibits a good coordinating power (NO_3^- for instance), or by abstraction of F^- from PF_6^- (as in complex IX). It should be noted that the monocation (corresponding to VIII) cannot be obtained even when the ratio Ag^+/complex ion is 1/1. In this last case, we observed only a mixture of the oxidized product (VIII or IX) with the starting material.

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